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## PATENT SPECIFICATION

DRAWINGS ATTACHED

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### COMPLETE SPECIFICATION

#### Production of Finely Divided Titanium Dioxide

5 We, SAUREFABRIK SCHWEIZERHALL, Schweizerhalle, Kanton Baselland, Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention is an improvement of the process for production of pigmentary titanium dioxide by the decomposition of vapourised titanium tetrachloride with gases containing free oxygen at high temperatures.

15 A special object of this invention is concerned with the manufacture of pigmentary rutile titanium dioxide, in which at least 90% of the product consists of the rutile crystal modification and the rutile has an average particle size of about 0.5 microns or less.

20 One known method of decomposing titanium tetrachloride with gases containing free oxygen consists in separately preheating titanium tetrachloride and gases containing free oxygen up to decomposition temperature and mixing those gases in a reaction chamber. In Specification No. 258,313 there are described methods of producing finely divided oxides of metals or silicon, which include distributing volatile metal or silicon halides and separately added volatilizable or gaseous combustible matter in an oxidising gas, igniting to form a flame and separating the resulting oxide from the gaseous products of combustion. Examples of the halogenides given are ferric chloride, 35 chromyl chloride, aluminium chloride, silicon tetrachloride, titanium chloride or mixtures of such compounds.

In Specification No. 535,214 there are described methods of producing titanium dioxide

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by thermal decomposition of vapourised titanium halide, preferably the tetrachloride in the presence of an oxidising gas characterised in that the reaction mixture is maintained remote from hot surfaces during such decomposition by creating and interposing therebetween a screen or blanket of inert or non-oxidising atmosphere separately introduced. It is stated that temperatures may be widely varied, that lower temperatures give lower yields, that it is usually found that a suitable product may be produced with maximum yield at temperatures from 1500—1850° F and that higher temperatures may be used but appear to increase the production of large crystals unsuitable for use as a pigment. 40 45 50 55

Examples are given of producing titanium dioxide alone followed by the statement that the titanium dioxide is usually in the form of a fine fluffy dust or powder apparently having the crystalline form of rutile. Thereafter it is stated it may be desirable to form a composite pigment by decomposing the titanium tetrachloride in the presence of another finely divided pigment or extender. The presence of small quantities of silica is said to modify the particle size. It is also proposed that zinc vapour, aluminium compounds such as aluminium chloride, iron compounds such as ferric chloride, antimony, tin, lead or bismuth compounds may be introduced and converted into their respective oxides during decomposition of the titanium chloride. It is also suggested that the second pigment or material from which the pigment is to be produced may be introduced during the later stages of oxidation of the titanium chloride, or after oxidation of the titanium compound is complete. 60 65 70 75

It is also proposed that the silica may be

Prior

77100 6

prepared from silicon tetrachloride; but it is suggested that this should be done before conversion of the titanium chloride.

5 In U.S.A. Specification No. 2,333,948 there are described methods of producing blended pigments, particularly titanium pigments. It is stated that, for example, white pigments may be prepared by thermal decomposition of a mixture of titanium tetrachloride and zinc chloride, aluminium chloride or silicon tetrachloride. Other halides are also suggested as additives. The temperatures suggested are 1400—2200° F.

15 Another method disclosed in Specification 661,685 consists in first preparing a mixture of titanium tetrachloride vapours and gases containing free oxygen suitably preheating the same and allowing it to flow into a reaction chamber wherein the mixture is continuously contacted with an auxiliary flame sustained by a separate inflow of combustible gas so as to 20 ignite the reactive mixture and maintain it in a flaming state. This auxiliary flame may, for instance, be sustained by the combustion of carbon monoxide or hydrogen in gases containing free oxygen. The auxiliary flame can be carried out by introducing the combustible gas concentrically around the reaction gas mixture in the reaction chamber. This is true also of 25 the gases containing free oxygen, which in part at least may be supplied separately from the reaction mixture. In this way, a constantly burning auxiliary flame, in which the reaction mixture uniformly ignites and burns with production of a flame, exists around the stream of reaction gas.

35 In the decomposition of titanium tetrachloride, according to the process of the said specification 661,685, the particle size of the resulting titanium dioxide depends on the decomposition conditions. Thus the concentration of the titanium tetrachloride vapour in the reaction gas mixture, the flame temperature and the type of gas feed, all play important 45 roles. In order to obtain titanium dioxide of very great fineness, it is advantageous to carry out the decomposition very vigorously according to the known physical-chemical conditions of crystal formation; in this way the particles, which are formed first, are afforded 50 no opportunity for further growth. In carrying out the process on a large scale, however, difficulties can appear in this respect, because the large amounts of reaction mixture used, that is, the mixture of oxygen-containing gas and titanium tetrachloride vapour, cannot be heated to the reaction temperature with sufficient rapidity as easily as they can be on a small scale.

60 In the thermal decomposition of titanium tetrachloride vapour with gases containing free oxygen, the titanium dioxide is produced principally in the anatase form or in mixtures of anatase and small amounts of rutile. In 65 another patent application No. 23454/50

(Serial No. 673,782), a method is described by means of which a titanium dioxide with a rutile content of at least 40—60% by weight can be obtained. This method consists essentially in allowing a mixture of titanium tetrachloride vapour and oxygen-containing gas to pass into the reaction chamber in the form of a thin layer of gas of, at most, 1 cm. thickness and advantageously, to likewise ignite it to a flame by means of an auxiliary flame produced from the combustible gas and oxygen-containing gas and surrounding the reaction gas mixture.

Our patent 686,570 describes and claims:—  
‘A process for the production of pigmentary titanium dioxide at least about 90% of the product consisting of the rutile crystal modification by the thermal decomposition of vaporised titanium tetrachloride with gases containing free oxygen under flame-producing conditions, which comprises the steps of discharging a uniform pre-mixture of titanium tetrachloride vapours, gases containing free oxygen and a volatile aluminium compound which is converted into  $Al_2O_3$  under the conditions of the process, into a combustion zone, the amount of aluminium compound being such that the  $TiO_2$  produced contains 0.01 to 10% by weight of  $Al_2O_3$ , said mixture being at a temperature above the dew point of the titanium tetrachloride in the said mixture but not exceeding 500° C. and continuously contacting said uniform premixture with an auxiliary flame sustained by a separate inflow of combustible gas so as to ignite the reaction mixture and maintain it in a flaming state.’—and our patent 686,568 describes and claims:—‘A process for the production of pigmentary titanium dioxide by the thermal decomposition of vaporised titanium tetrachloride with gases containing free oxygen under flame-producing conditions, which comprises the steps of discharging a uniform pre-mixture of titanium tetrachloride vapours, gases containing free oxygen and a volatile silicon compound which is converted into  $SiO_2$  under the conditions of the process, into a combustion zone at a linear flow rate of 1 to 50 meters per second, the amount of Si compound being such that the  $TiO_2$  produced contains 0.01 to 10% by weight of  $SiO_2$ , said mixture being at a temperature above the dew point of the titanium tetrachloride in the said mixture but not exceeding 500° C. and continuously contacting said uniform premixture with an auxiliary flame sustained by a separate inflow of combustible gas so as to ignite the reaction mixture and maintain it in a flaming state.’

According to the present invention we provide a process for the production of pigmentary rutile  $TiO_2$  in which at least 90% of the product consists of the rutile crystal modification and the rutile has an average particle size of about 0.5 microns or less, by the thermal decomposition of vaporised  $TiCl_4$  with

gases containing free oxygen under flame producing conditions, which includes decomposing with oxygen,  $\text{TiCl}_4$  vapours containing an added amount of a volatile silicon compound and an added amount of a volatile aluminium compound which are converted into  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  respectively under the conditions of the process, the amount of silicon and aluminium compound being such that the  $\text{TiO}_2$  product contains 0.5 to 5% by weight of  $\text{SiO}_2$  and 0.5 to 5% by weight of  $\text{Al}_2\text{O}_3$ , the ratio of  $\text{Al}_2\text{O}_3:\text{SiO}_2$  in the product being 3:1 to 1:1 by weight, and maintaining the temperature during the decomposition with the range of  $1000^\circ\text{C}.$ — $1600^\circ\text{C}.$

The addition of the aluminium compound itself influences to a certain degree, the particle size of the titanium dioxide that forms, since a somewhat coarser particle results than without the addition.

This undesirable effect on the particle size of the rutile product is overcome by the addition to the  $\text{TiCl}_4$ , in addition to the volatile aluminium compound, of a small amount of a volatile silicon compound. While the method in which the volatile silicon compound functions is not known, it appears to serve as a seeding agent during the formation of the  $\text{TiO}_2$  and thus permits the production of the aforementioned extremely small and uniform pigment particles. On the other hand, the volatile aluminium compound apparently serves as a rutile promoter. The addition of small amounts of the silicon compound is sufficient appreciably to decrease the particle size of the product. An amount of silicon compound is employed such that the  $\text{TiO}_2$  product contains 0.5—5% by weight of  $\text{SiO}_2$ . For most purposes, however, it will be found that 0.5 to 2% by weight of  $\text{SiO}_2$  is sufficient to obtain the desired particle size distribution. On the other hand, while amounts of silicon compound in excess of 5%, based on the  $\text{SiO}_2$  content of the product, may be employed, they are considered to be outside the scope of this information as these excessive amounts may have a disadvantageous effect because the volatile silicon compounds always tend to suppress to a certain degree the formation of rutile  $\text{TiO}_2$ . A high enough amount of volatile aluminium compound therefore has to be added to overcome this influence.

The amount of aluminium-containing material to be added in order to get a rutile content of about 90% and more depends also on the method of carrying out the decomposition. In order to reach the maximum rutile content, such an amount of aluminium compound that the titanium dioxide obtained contains 0.5—5%, preferably 0.5 to 2% by weight of aluminium oxide is used.

Aluminium compounds which may be employed as rutile-promoting agent according to the present invention may be inorganic in character, as for example an aluminium halide

such as aluminium chloride, or they may be organic in character, as for instance trimethyl aluminium etc.

Volatile silicon compounds which may be employed as crystal growth-controlling agent according to the present invention may be inorganic in character, for instance a silicon halide containing a halogen with an atomic weight of at least 35 such as silicon tetrachloride ( $\text{SiCl}_4$ ), silicon hexachloride ( $\text{Si}_2\text{Cl}_6$ ), silicon tetrabromide, silicon chloroform ( $\text{SiHCl}_3$ ) etc., or they may be organic in character, for instance, a silicon ester such as silicon tetra-ethyl ester [ $\text{Si}(\text{OC}_2\text{H}_5)_4$ ] or organic silicane such as chloromethylsilane ( $\text{SiH}_2\text{CH}_2\text{Cl}$ ), dimethylsilane [ $\text{SiH}_2(\text{CH}_3)_2$ ], tetraethylsilane [ $\text{Si}(\text{C}_2\text{H}_5)_4$ ] etc. Advantageously, a volatile silicon compound is employed which has a low boiling-point, such as for example silicon tetrachloride or silicon hydride ( $\text{SiH}_4$ ).

If volatile aluminium halide compounds, added as volatile halides such as anhydrous aluminium chloride, are added to the titanium tetrachloride vapour, the addition can be done in such a way that a fixed amount of solid aluminium chloride is dissolved in the liquid titanium tetrachloride to be vaporised. According to the concentration of the dissolved aluminium chloride, there is then obtained a definite concentration of aluminium chloride in the titanium tetrachloride vapour. The highest concentration of aluminium chloride can be obtained when a titanium tetrachloride solution is used which is saturated, when hot, with aluminium chloride. The concentration of the aluminium chloride in the vapour over a solution of  $\text{TiCl}_4$  saturated with it amounts to, according to the temperature of the  $\text{TiCl}_4$ , from 0.5 to 1.5% by weight of titanium tetrachloride. But the aluminium chloride can also be added to the titanium tetrachloride vapour or to the titanium tetrachloride vapour-oxygen mixture separately by subliming the  $\text{AlCl}_3$  either directly from an auxiliary vessel or, better still, by preparing it only shortly before the addition to the titanium tetrachloride vapour. In the latter case, it is advantageous to pass chlorine gas, alone or in admixture with diluent, over heated, metallic aluminium, for example in the form of shavings, and then to combine the reaction product, consisting of aluminium chloride vapour and, in some cases, inert gas, with the titanium tetrachloride vapour or the titanium tetrachloride-oxygen gas mixture. Aluminium oxide may be used instead of metallic aluminium; in such case use is made of a mixture of CO and  $\text{Cl}_2$  or phosgene for the chlorination; or use can be made of a mixture of aluminium oxide and carbon and chlorination carried out with elemental chlorine.

The aluminium halide added should preferably have a very low content of ferric halide. If the ferric halide content is too high the produced titanium dioxide will be off colour

and light sensitive due to small amounts of iron oxide being formed out of the ferric halide vaporised together with the aluminium halide. To prevent a disadvantageous discoloration, the aluminium halide should contain less than 1% preferably less than 0.1% by weight of ferric halide.

Since anhydrous silicon tetrachloride is miscible in all proportions with titanium tetrachloride, when silicon tetrachloride, as silicon containing compound is mixed with aluminium chloride for the formation of rutile, a vaporous mixture can be obtained directly by vaporisation of the three mixed chlorides. But one can also proceed in the same way as in the case of aluminium chloride by mixing the titanium tetrachloride vapour or the titanium tetrachloride vapour-oxygen mixture, aluminium chloride and silicon chloride vapours one after the other or jointly, whether one vaporises the liquid silicon chloride separately, or prepares the silicon chloride from silicon and chlorine directly before mixing it with the  $TiCl_4$ .

It is important in the feed of the reaction mixture to maintain the component in vaporous condition. Preferably, therefore, according to the present invention the vaporous mixture is further heated to a temperature somewhat in excess of the dew point of the  $TiCl_4$ .  $TiCl_4$  vapour ordinarily condenses at about  $136^\circ C$ . but this condensation point will vary under the influence of additional gases such as the aluminium and silicon halides and oxygen. It is a feature of the present invention to heat the reaction mixture to a temperature of about  $135^\circ C$ . or higher in order to prevent the condensation of  $TiCl_4$  prior to its introduction into the reaction zone. This prevents any droplets of  $TiCl_4$  from entering the reaction zone, which droplets will be thermally decomposed at a much slower rate than the gaseous components and will thus result in the formation of coarse rutile  $TiO_2$  particles which are non-pigmentary in character. The practical maximum to which the reaction mixture is preheated according to the present invention is about  $500^\circ C$ ., whereby premature oxidation of the  $TiCl_4$  is avoided.

A further important feature of the present invention resides in the utilisation of an auxiliary flame with which the reaction mixture is continuously contacted. The auxiliary flame is obtained by introducing separately from the reaction mixture a combustible gas and a free oxygen-containing gas in such proportions and amounts that the resulting auxiliary flame burns independently in the absence of the reaction mixture i.e. the production of the auxiliary flame does not depend upon the oxygen supplied to the reaction mixture whether or not the oxygen in the reaction mixture, when present, assists the combustion of the separately introduced combustible gas. This auxiliary flame is sustained by a combustion reaction, such as for example the burning

of methane, acetylene, hydrogen or the like commercially available gases and gaseous mixtures. A particularly suitable and presently preferred manner of combustion consists in burning carbon monoxide and oxygen, the carbon monoxide preferably being obtained as a by-product of the chlorination of titanium-bearing ores and slags.

A special advantage of the employment of the carbon monoxide-oxygen combustion for the auxiliary flame resides in the fact that the gaseous end-products consist of chlorine, carbon-dioxide, excess oxygen and inert diluents. In contradistinction to this, the burning of gases which contain free or combined hydrogen results in the formation, additionally, of hydrogen chloride. The presence of appreciable quantities of the latter complicates the recovery of the chlorine to be re-used for chlorination purposes, inasmuch as it becomes necessary to recover the same from the hydrogen chloride.

By regulating the ratio of the amount of combustible gas, for instance of carbon monoxide, to the amount of  $TiCl_4$ , the temperature of the decomposition can easily be controlled. It is an important feature of the present invention for the production of rutile pigmentary  $TiO_2$  to maintain the temperature during the decomposition within the range  $1000^\circ C$ .— $1600^\circ C$ . Temperatures above  $1600^\circ C$ . are likely to cause dissociation of the  $TiO_2$ . Temperatures below  $1000^\circ C$ . tend to suppress the formation of rutile in favour of the anatase crystal modification of  $TiO_2$  even in the presence of aluminium compounds.

Preferably the ratio of the amount of combustible gas to  $TiCl_4$ , for instance of carbon monoxide to  $TiCl_4$ , is adjusted to at least 0.25 to 1.5 mole CO per mole  $TiCl_4$ . The combustion reaction of such a combustible gas proceeds at very high flame temperatures of more than  $1500^\circ C$ . and up to  $2000^\circ C$ . Thus the temperature of the auxiliary flame is sufficiently high that the gaseous reaction mixture is rapidly heated to the very high temperatures which are necessary to produce  $TiO_2$  consisting predominantly of rutile while at the same time preventing excessive growth of the pigment particles.

In carrying out the decomposition of the titanium chloride-oxygen mixture, it is important to control the feed rate of the reaction mixture to insure that complete decomposition thereof is effected within the area of the auxiliary combustion reaction. To this end, a maximum linear flow rate of 50 meters per second insures complete decomposition of the reaction mixture while preventing excessive titanium dioxide crystal growth. If this maximum rate of flow is exceeded, a portion of the reaction mixture may pass beyond the combustion zone and a part of the titanium tetrachloride may be oxidised still in the gaseous phase but in the presence of already formed titanium di-

oxide crystals. This results in crystal-twinning and particle growth to such an extent that the product is non-uniform and unfit for use as a pigment. However, the feed rate should be not less than 1 m/second in order to prevent undesired deposition of  $\text{TiO}_2$  and clogging at the gas inlets.

The invention is not necessarily bound up with a premix of oxygen and titanium chloride. One can e.g. also decompose a gaseous mixture of titanium chloride with volatile aluminium compound and volatile silicon compound preheated up to  $1000^\circ\text{C}$ . with an oxygen containing gas preheated up to  $1000^\circ\text{C}$ . However, the use of a mixture of titanium tetrachloride with vaporised aluminium compound, vaporised silicon compound and with oxygen containing gas is very advantageous for the attainment of the desired effect i.e. the formation of a high quality rutile. The reaction of titanium-tetrachloride vapour and oxygen being exothermic, a further amount of heat is developed in the flame when the decomposition reaction of the titanium-tetrachloride starts. If the oxygen for the decomposition is e.g. in a homogeneous mixture with the tetrachloride the decomposition can proceed very rapidly. Therefore the heat is developed in the small space where the decomposition of the whole chloride takes place, thus producing a further increase of temperature. As the solid titanium dioxide particles formed dissipate a large amount of heat by radiation it is important to effect the decomposition as rapidly as possible in order to attain the desirable increase of temperature. This rapid decomposition can be attained perfectly if the chloride enters already uniformly premixed with the oxygen. If this is not the case most of the heat of reaction during the mixing time of the chloride with the oxygen. The vaporised aluminium compound being introduced also in a homogeneous dispersion in oxygen containing gas is able to act as a promoter for the formation of the rutile lattice because it is converted to aluminium-oxide at the same time as is the titanium chloride and above all because it acts as set forth in an extremely hot decomposition zone. The vaporised silicon compound if premixed with the oxygen containing gas too is able to act as seeding agent for the  $\text{TiO}_2$  production and as a stabiliser in the most perfect way, because the silicon compound can find the oxygen necessary for its decomposition already in molecular dispersion. By applying such a premixture the formation of a fine and very uniform grain is obtained.

The mixture should therefore preferably contain at least 50% of the oxygen necessary for the decomposition of the titanium-tetrachloride but advantageously the mixture contains the stoichiometrical amount of oxygen or even a surplus of 30 to 100%. If the mixture does not contain the sufficient amount of oxy-

gen for the decomposition of the  $\text{TiCl}_4$ , the remaining oxygen has to be fed separately, preferably together with the oxygen for the auxiliary combustion reaction.

The mixture may contain besides titanium-tetrachloride, volatile aluminium compound, volatile silicon compound and oxygen, also an inert gas such as nitrogen and carbon dioxide. The addition of inert gases affects the particle size of the titanium dioxide produced. An increasing dilution of the mixture with inert gas will decrease the particle size.

The above described method for preparing the mixture all result in the preparation of uniform mixtures producing the desired effects.

The rutile pigment produced according to the invention contains a small amount of chlorine and hydrogen chloride in the voids and on the surface of the particles. After driving off these gases, for instance by evacuation and neutralization for instance with a small amount of lime, the product can be used directly as a pigment without any calcination and milling operation. For special purposes it might be desirable to subject the product before or after neutralization to an after-treatment process such as classification, surface treatment and the like finishing treatments known in the art.

By using pure metallic chlorides containing only very slight amounts of iron and vanadium chlorides, a rutile pigment of pure white colour is obtained by the method of the present invention. The colour and tinting strength characteristics of the product are considerably improved compared with those of the rutile pigments prepared according to the commercially accepted sulphuric acid or hydrochloric acid hydrolysis of titanium solutions.

It is known e.g. from British Specification 567,093 as open to public inspection under Sec. 91(4) of the Patents Acts 1907—1946 that the pigment characteristics of titanium dioxide produced by decomposition of titanium chloride vapour with oxygen can be improved by the addition of small amounts of a halide of a metal of the group consisting of Cr, Si, Al, Zr, Sb, Zn, Be, B, Cd, Co, Mo, Ni and V.

It was surprising to find that the combined action is working in the mentioned desired direction because aluminium not only favours the formation of rutile but also the formation of coarse crystals and silicon not only the formation of fine crystals but also stabilizes the anatase modification.

The process according to the present invention can be carried out with a wide variety of apparatuses. Use may advantageously be made, for example, of the construction according to the accompanying drawing. It will be understood, however, that other suitable forms of apparatus may be used equally as well. The drawing shows diagrammatically a vertical

longitudinal section through a reaction chamber suitable for carrying out the process.

As shown, the device for carrying out such process may consist in general of a reaction chamber formed by heat insulated walls (a) which may be heated externally by an electric resistance heater arranged between the walls and the insulation and a reactant gas supply device (b) in the form of three concentric conduits. The reaction gas mixture is supplied through the central conduit, the oxygen or gases containing free oxygen through the outermost conduit, and the CO or other combustible gas through the intermediate conduit. The device may additionally comprise a funnel (e) serving to carry away the precipitated titanium dioxide, and an exhaust opening (f) for drawing off the produced crude gases which, in view of their content of titanium dioxide, may advantageously be delivered to a dust-extracting plant.

The following examples, wherein the parts and percentages are by volume, unless otherwise stated, are intended to be illustrative, but not at all limitative, of the invention, and are intended to exemplify presently preferred embodiments thereof.

#### EXAMPLE 1.

Over pure aluminium turnings containing less than 0.1% by weight Fe, a stream of chlorine and nitrogen 1:2 is conducted at a temperature of about 400° C. The vaporised reaction product is added to a vaporised mixture of 1 vol.  $\text{TiCl}_4$ , 1.5 vol.  $\text{O}_2$  and 1.5 vol.  $\text{N}_2$  and a temperature of 150° C. and the rate of the chlorine adjusted in such a way as to attain a concentration of  $\text{AlCl}_3$  in the mixture of 5% by volume calculated on the volume of  $\text{TiCl}_4$ . To this mixture a mixture of silicon chlorides is added obtained by chlorinating pure Si with  $\text{Cl}_2$  at 500° C., the chlorine rate being adjusted in such a way that the concentration of silicon chlorides is 4% by volume calculated on the volume of  $\text{TiCl}_4$ . For the decomposition an ignition device consisting of three concentric tubes is used and a reaction chamber suitable for carrying out the process of the invention, for example a reaction chamber as shown in the accompanying drawing. The reaction mixture enters the reaction chamber through the central tube 1 with a velocity of 20 m/sec. Through the passage between tubes 1 and 2 a mixture of 60% CO, 10%  $\text{H}_2$  and 30%  $\text{N}_2$  is introduced with a velocity of 300 cm/sec. and through passage between tubes 2 and 3 oxygen with a velocity of 200 cm/sec. The ambient temperature outside the flame annulus is kept at about 1050° C. A titanium dioxide with a rutile content of more than 95% by weight, a colour of 105 and a tinting strength of 1650 is obtained.

#### EXAMPLE 2.

To a still, a warm solution of 2.2% per weight of aluminium-chloride (containing less than 0.1% by weight,  $\text{FeCl}_3$ ) and 1.2% per

weight of silicon chloride in titanium-chloride is fed continuously. The still is kept at a temperature of about 105° C. and pure oxygen is bubbled continuously through this solution. To 2.5 volumes of the vapourous mixture preheated afterwards to 150° C., 1.5 volumes of nitrogen preheated to 150° C. are added. For the decomposition an ignition device consisting of 5 concentric tubes is used and a reaction chamber as described in example 1. The sizes of the concentric tubes are as follows: Tube 1: 20—22 mm, tube 2: 26—29 mm, tube 3: 39—42 mm, tube 4: 52—55 mm and tube 5: 60—64 mm. Through the central tube 1 is fed: 18 litres/min. of CO, through the passage between the first and the second tube: 9 litre/min. of  $\text{O}_2$ , through the passage way between the third and second tube: 160 litre/min. of the chloride/oxygen/nitrogen mixture, through the passage between tubes 3 and 4: 40 litre/min. of CO and in the outermost passage 20 litre/min. of oxygen. The gases fed directly next to the titanium chloride mixture i.e. the gases fed through the passage between tubes 1 and 2 and through the passage between 3 and 4 have a moisture content of at most 0.1 gr  $\text{H}_2\text{O}/\text{m}^3$ . To ensure the burning of the CO-flame the carbon monoxide flame is ignited before starting the introduction of the chloride mixture and is kept burning as long as the mixture is fed to the chamber. The temperature outside the exterior flame annulus ambient to the flame is kept at 1200° C. A very uniform  $\text{TiO}_2$  with a particle size of about 0.3 micron, a colour value of 108 and a tinting strength of 1650 is continuously produced. The gases loaded with the pigmentary titanium dioxide are withdrawn by an exhaust opening and freed from the titanium dioxide by an electrostatic dust extracting apparatus.

#### EXAMPLE 3.

On the top cover of a reaction chamber as in example 1 a plurality of ignition devices, each consisting of three concentric tubes are assembled. The tubes of each of the single ignition devices have the following dimensions: tube 1: 4—6 mm; tube 2: 10—12 mm and tube 3: 14—16 mm. Through each of the central tubes a mixture consisting of 1 volume of  $\text{TiCl}_4$ , 0.8 vol.  $\text{O}_2$ , 0.8 vol.  $\text{N}_2$ , 0.007 vol. of  $\text{SiHCl}_3$  and 0.02 vol. of  $\text{AlBr}_3$  (having an iron content of less than 0.1% by weight) at a temperature of 150° C. is introduced with a velocity of 150 m/sec. Through the passage between tubes 2 and 1 pure carbon-monoxide with a maximum water content of 0.1 gr  $\text{H}_2\text{O}/\text{m}^3$  is introduced with a velocity of 200 cm/sec. and through the passage between 3 and 2 oxygen with a velocity of 250 cm/sec. A titanium dioxide with 98% by weight of rutile, a tinting strength of 1630 and a colour of 107 is produced, if the ambient temperature outside the flame annulus is kept at 1200° C.



## EXAMPLE 4.

A supply device consisting of three concentric tubes with the following dimensions is used. Central tube 6—8 mm, intermediate tube 12—14 mm and outermost tube 16.5—18 mm. Thus the following cross-section areas for the incoming gases are provided: central tube 28 mm<sup>2</sup>, intermediate passage 62 mm<sup>2</sup> and outermost passage 60 mm<sup>2</sup>. The ignition device is set to work at the top of a reaction chamber as described in example 1. Through the central tube is introduced with an exit velocity of 2 m/sec. a mixture of about 1 volume TiCl<sub>4</sub> vapour, 0.05 volumes of AlCl<sub>3</sub>, 0.05 volumes of SiCl<sub>4</sub>, 0.85 volumes O<sub>2</sub> and 1. volume of N<sub>2</sub> prepared by admixing the required amount of AlCl<sub>3</sub> and SiCl<sub>4</sub> vapour obtained out of a sublimation chamber and a still respectively to the previously prepared and preheated TiCl<sub>4</sub>/O<sub>2</sub>/N<sub>2</sub> mixture. Through the intermediate passage is introduced a gas mixture consisting of 80% CO and 20% H<sub>2</sub> with an exit velocity of 100 cm/sec. and through the outermost passage pure oxygen with a velocity of 150 cm/sec. The temperature outside the flame annulus of the atmosphere ambient to the flame was held at about 1300° C. A titanium dioxide is obtained with an average particle size of about 0.4μ, a rutile content of about 90% by weight and a tinting strength of about 1550. Instead of SiCl<sub>4</sub> the corresponding amount of e.g. Si<sub>2</sub>Br<sub>6</sub>, SiI<sub>4</sub> or Si<sub>2</sub>Cl<sub>6</sub> and instead of AlCl<sub>3</sub> the corresponding amounts of e.g. AlBr<sub>3</sub> or AlI<sub>3</sub> can be added.

## EXAMPLE 5.

The same apparatus as in example 1 is used. To a mixture of 1 volume TiCl<sub>4</sub>, 1.5 volumes of O<sub>2</sub>, 0.02 volumes of AlCl<sub>3</sub> and 2.5 volumes of N<sub>2</sub>, gaseous SiH<sub>2</sub>ClCH<sub>3</sub> is added so as to obtain a ratio of 1 volume of TiCl<sub>4</sub> to 0.01 volume of SiH<sub>2</sub>ClCH<sub>3</sub>. The exit velocity of the mixture through the central tube is kept at about 7.5 m/sec. Through the intermediate passage pure CO loaded with 2.5% volume of gasoline is fed with an exit velocity of 150 cm/sec. and is burned with pure oxygen entering the reaction chamber through the outermost passage with a velocity of 150 cm/sec. The temperature outside the flame annulus is kept at about 1300° C. A titanium dioxide with a particle size between 0.3 and 0.8 and a tinting strength of about 1600 is obtained.

## EXAMPLE 6.

A supply device consisting of three concentric tubes with the following dimensions is used: Central tube 4/6 mm, intermediate tube 10/12 mm and outermost 14/16 mm. The same chamber as in example 1 is used. Through the central tube a mixture of 1 volume TiCl<sub>4</sub>, 1.3 volumes of O<sub>2</sub>, 1.3 volumes CO<sub>2</sub>, 0.03 volumes of AlCl<sub>3</sub> and 0.03 volumes of SiHCl<sub>3</sub> is discharged with an exit velocity of 40 m/sec. Through the intermediate tube pure oxygen is discharged with a velocity of 300 cm/sec. and through the outermost tube

a mixture of 10% CH<sub>4</sub> and 90% CO with a velocity of 300 cm/sec. The temperature outside the flame annulus is kept at about 1050° C. The titanium-dioxide obtained has an average particle size of about 0.5 μ and a tinting strength of about 1550.

The commercial available rutile pigments have colour values of from 85 to 95 and tinting strength of from 1350 to 1550 if evaluated by the same method.

## WHAT WE CLAIM IS:—

1. A process for the production of pigimentary rutile TiO<sub>2</sub>, in which at least 90% of the product consists of the rutile crystal modification and the rutile has an average particle size of about 0.5 microns or less, by the thermal decomposition of vaporised TiCl<sub>4</sub> with gases containing free oxygen under flame producing conditions, which includes decomposing, with oxygen, TiCl<sub>4</sub> vapours containing an added amount of a volatile silicon compound and an added amount of a volatile aluminium compound which are converted into SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> respectively under the conditions of the process, the amount of silicon and aluminium compound being such that the TiO<sub>2</sub> product contains 0.5 to 5% by weight of SiO<sub>2</sub> and 0.5 to 5% by weight of Al<sub>2</sub>O<sub>3</sub>, the ratio of Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> in the product being 3:1 to 1:1 by weight, and maintaining the temperature during the decomposition within the range of 1000°—1600° C.

2. A process for the production of pigimentary rutile TiO<sub>2</sub>, in which at least 90% of the product consists of the rutile crystal modification and the rutile has an average particle size of about 0.5 microns or less, by the thermal decomposition of vaporised TiCl<sub>4</sub> with gases containing free oxygen, which includes the steps of discharging a uniform premixture of TiCl<sub>4</sub> vapours, gases containing free oxygen and a volatile silicon compound and a volatile aluminium compound, which are converted into SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> respectively under the conditions of the process, into a combustion zone, the amount of silicon and aluminium compound being such that the TiO<sub>2</sub> product contains 0.5 to 5% by weight of SiO<sub>2</sub> and 0.5 to 5% by weight of Al<sub>2</sub>O<sub>3</sub>, the ratio of Al<sub>2</sub>O<sub>3</sub>:SiO<sub>2</sub> in the product being 3:1 to 1:1 by weight, said mixture being above the dew point of the TiCl<sub>4</sub> in the said mixture but not exceeding 500° C., continuously contacting the said uniform pre-mixture with an auxiliary flame that is a flame obtained by introducing separately from the reaction mixture a combustible gas and a free oxygen-containing gas in such proportions and amounts that the resulting auxiliary flame burns independently in the absence of the reaction mixture, so as to ignite the reaction mixture and maintain it in a flaming state and maintaining the temperature during the decomposition within the range 1000°—1600° C.

3. A process as claimed in claim 1 or claim

2 in which the amount of silicon compound and aluminium compound are such that the  $\text{TiO}_2$  product contains 0.5 to 2% by weight of  $\text{SiO}_2$  and 0.5 to 2% by weight of  $\text{Al}_2\text{O}_3$ .

5 4. A process claimed in claim 2 or claim 3 in which the uniform vaporous premixture of titanium tetrachloride vapour, gases containing free oxygen, volatile silicon compound and volatile aluminium compound is discharged to  
10 the reaction chamber with a linear flow rate of 1—50 meters per second.

5. A process claimed in any one of claims 2 to 4 in which the uniform vaporous premixture of titanium tetrachloride vapour, gases  
15 containing free oxygen, volatile silicon compound and volatile aluminium compound and the gases for the auxiliary flame are discharged into the reaction chamber in streams lying one within another.

20 6. A process as claimed in any of the preceding claims in which as volatile silicon compound a volatile silicon halide is used wherein the halogen has an atomic weight of at least 35.

25 7. A process as claimed in any of the preceding claims in which as volatile aluminium compound a volatile aluminium halide is used.

8. A process claimed in any one of claims 1 to 5 or in claim 7 in which as volatile silicon  
30 compound a volatile organic silicon compound is used.

9. A process claimed in any one of claims 1 to 6 or in claim 8 in which as volatile aluminium compound an organic volatile aluminium  
35 compound is used.

10. A process claimed in any one of claims 2 to 9 in which the uniform vaporous premixture of titanium tetrachloride vapour, gases containing free oxygen, volatile silicon  
40 compound and volatile aluminium compound contains at least the stoichiometrical amount of

oxygen for the decomposition of the titanium tetrachloride.

11. A process claimed in any one of claims 2 to 10 in which the uniform vaporous premixture of titanium tetrachloride vapour, gases containing free oxygen, volatile silicon compound and volatile aluminium compound is ignited and decomposed by the aid of the combustion of carbon monoxide and oxygen.

12. A process claimed in claim 11 in which the molar ratio of the carbon monoxide used in the auxiliary flame to the titanium tetrachloride vapour is from 0.25 to 1.5.

13. A process claimed in claim 6 or claim 7 in which aluminium chloride and silicon chloride are vaporised together with titanium tetrachloride out of a warm solution of aluminium chloride and silicon chloride in titanium tetrachloride.

14. A rutile  $\text{TiO}_2$  pigment consisting essentially of a major proportion, in excess of 90% of the  $\text{TiO}_2$  in the rutile modification thereof and containing in addition thereto from 0.5% to 5% by weight of  $\text{SiO}_2$  and from 0.5% to 5% of  $\text{Al}_2\text{O}_3$  by weight in the  $\text{TiO}_2$  crystal lattices, the ratio by weight of  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  being from 3:1 to 1:1, said rutile being characterised by an average particle size of about 0.5 microns or less.

15. A rutile  $\text{TiO}_2$  pigment claimed in claim 14 containing from 0.5% to 2% of  $\text{SiO}_2$  and from 0.5 to 2% of  $\text{SiO}_2$  and from 0.5 to 2% of  $\text{Al}_2\text{O}_3$ .

16. A rutile  $\text{TiO}_2$  pigment claimed in claim 14 or claim 15 whenever produced by any of the processes herein described and claimed.

MEWBURN, ELLIS & CO.,  
70 & 72, Chancery Lane, London, W.C.2,  
Chartered Patent Agents.



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1 SHEET

AMENDED SPECIFICATION

*This drawing is a reproduction of  
the Original on a reduced scale.*

